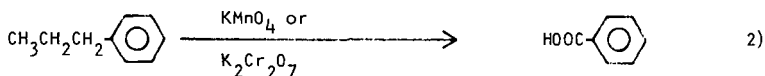
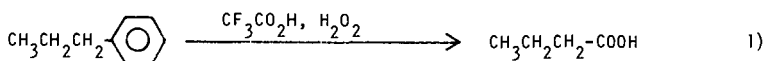


THE FATE OF SULFUR FUNCTIONS ON OXIDATION WITH PEROXYTRIFLUOROACETIC ACID

Clifford G. Venier, Thomas G. Squires, Yu-Ying Chen,
Juliana C. Shei, Robert M. Metzler, and Barbara F. Smith

Ames Laboratory*, Iowa State University, Ames, Iowa 50011

Oxidation has long been one of the primary tools used to probe the chemical structure of coal(1). The newest method is that developed by Deno, who reported that, while the aromatic portions of molecules were rapidly degraded by reaction with hydrogen peroxide in trifluoroacetic acid, the aliphatic skeleton is relatively inert to the reagent (2,3,4), equation 1). In contrast, classical oxidants, such as potassium permanganate or potassium dichromate, are known to preferentially oxidize the aliphatic portions of alkylated aromatics, equation 2). Deno claimed that this



new degradation will be useful in the determination of coal structure and has recently published structural studies based on peroxytrifluoroacetic acid oxidations (5-9).

We believe that this oxidation might be very useful in the determination of the kinds and amounts of organic sulfur functional groups in coal, based on the following considerations:

1. Of all the functionalities proposed for coal (see Figure 1), those containing divalent (sulfide) sulfur are likely to be the most nucleophilic.
2. With a powerfully electrophilic oxidant, such as peroxytrifluoroacetic acid, the most nucleophilic atoms, the sulfurs, will be the most readily oxidized.
3. The functionalities resulting from the oxidation of divalent sulfur, namely sulfones and sulfonic acids, are electron-withdrawing groups.
4. Since the mechanism of the electrophilic oxidation of aromatic rings involves the rings as sources of electrons, electron-withdrawing substituents, in particular, $-\text{SO}_2\text{R}$ and $-\text{SO}_3\text{H}$, will retard the oxidation of rings to which they are chemically attached.

On the basis of these assumptions, we would expect aromatic rings directly attached to sulfur in coal to survive less than exhaustive oxidation and appear in the products as sulfones and sulfonic acids. Since the rest of the aromatic structure of coal will be completely oxidized, the higher molecular weight portion of the products should be enriched in compounds containing sulfur (see Figure 2).

Table 1 shows that the assumption that sulfur compounds are rapidly oxidized is true for most sulfur functions. Dibenzothiophene and diphenyl disulfide are

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exceptions, but under the conditions reported by Deno, they, too, are oxidized to the tetravalent state. The oxidation of dibenzothiophene to its dioxide was also recently reported by Liotta and Hoff(10), who also found that pyridines are oxidized to their N-oxides by peroxytrifluoroacetic acid. That tetravalent sulfur-bearing rings are less susceptible to oxidation can be seen in Table 1. Benzenesulfonic acid, diphenyl sulfone and dibenzothiophene are not oxidized under conditions, 5 hours at 60°C, which, according to Deno, oxidize alkyl benzenes. The point is further illustrated in Table 2 which shows the fate of ω -phenylalkyl phenyl sulfides ($n=0-3$). Decreasing yields of sulfones and increasing yields of the ω -carboxyalkyl phenyl sulfones signal increasing amounts of oxidation of the ring remote from sulfur as n goes from 0 to 3.

We believe that the anomalously large amount of benzenesulfonic acid observed in the oxidation of phenylethyl phenyl sulfide ($n=2$) arises from a more facile elimination of benzenesulfonic acid from phenylethyl phenyl sulfone than from the corresponding sulfones in the other cases. Benzenesulfonic acid would disproportionate (11) or oxidize(12) or both under the reaction conditions to yield benzenesulfonic acid. In fact, phenyl benzenthioisulfonate, the other product of the disproportionation is also observed in the reaction mixture, even though it would be expected to be itself relatively easily oxidized to benzenesulfonic acid

Finally, the assumptions upon which we based our tentative hypothesis that the peroxytrifluoroacetic acid oxidation might be useful in the determination of the chemical nature of organic sulfur in coal having been demonstrated, we turned our attention to coal itself (Illinois #6) and its pyridine extract. Figure 3 shows two gc traces of the CH_2N_2 -methylated products from the oxidation of coal by peroxytrifluoroacetic acid. Both FID and sulfur sensitive FPD detector traces are shown. While we have not yet identified these materials, we have demonstrated that compounds containing sulfur can be identified among the products of the peroxytrifluoroacetic acid oxidation of coal.

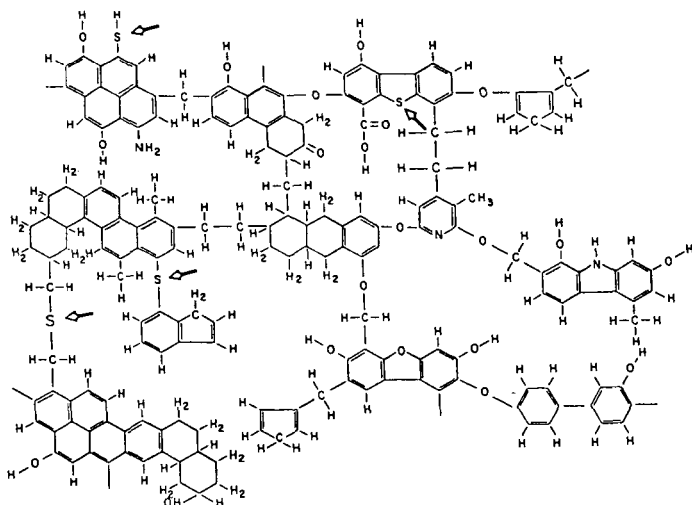


Figure 1. Modified Wiser Coal Structural Model

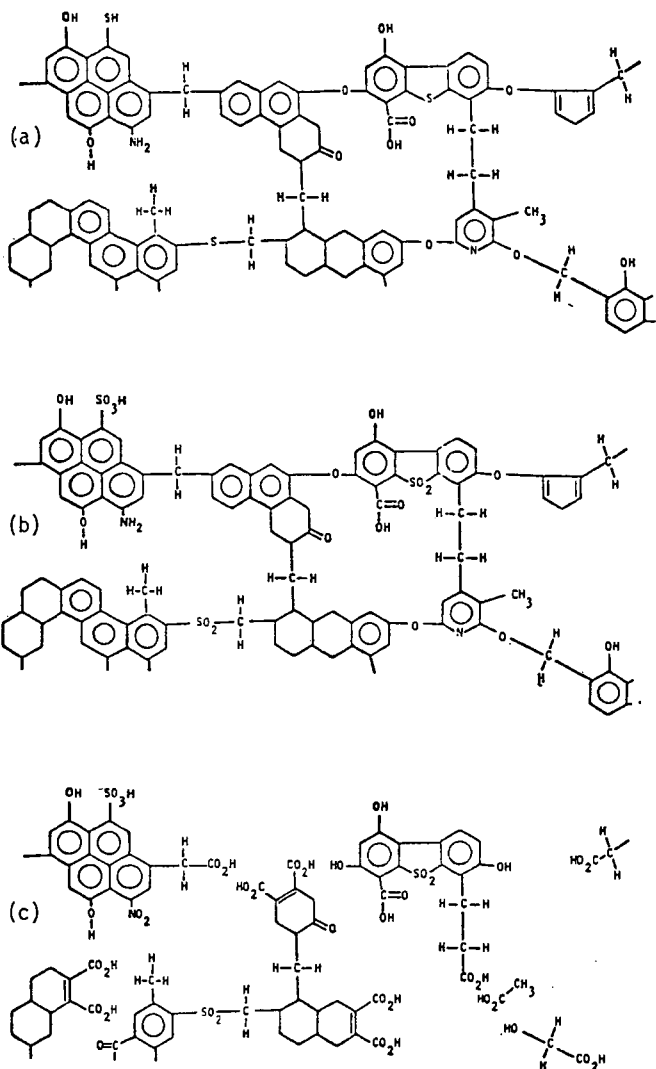


Figure 2. Proposed Effect of Peroxytrifluoroacetic Acid Oxidation on Coal Structure: (a) unmodified, (b) after partial oxidation, and (c) after extensive oxidation.

EXPERIMENTAL

All sulfides were used as obtained from commercial sources, except phenyl 2-phenyl-ethyl sulfide, which was prepared by the reaction of sodium benzenethiolate with 2-phenylethyl chloride. Trifluoroacetic acid, 30% hydrogen peroxide and 90% hydrogen peroxide were used as supplied. Infrared spectra were taken on a Beck Model 4230 or IBM FTIR/90 series spectrophotometer as KBr discs. Nuclear magnetic resonance spectra were taken at 60 MHz on a Varian Em-360A spectrometer.

Oxidation of Sulfides with Peroxytrifluoroacetic Acid: Trifluoroacetic acid and hydrogen peroxide were mixed at 0°C, the sulfide added with cooling, and the temperature of the reaction mixture adjusted to the desired temperature with a water bath. At the end of the reaction time, the reaction was poured into water and a small amount of platinum on asbestos or platinum on carbon was added to destroy excess peroxide. This step often required several hours. When the mixture proved negative to starch-KI paper, the excess trifluoroacetic acid and water was removed on a rotary evaporatory, the final vestiges of solvent and water removed at high vacuum on a vacuum line, and the mixture dissolved in methanol and treated with diazomethane in ether. The resulting mixture of neutral compounds and methylated acids was injected on to an OV 101/Chromasorb W-HP column (8'x1/4"). Compounds were identified by retention times and coinjection and quantitated by the internal standard method.

Oxidation of Coal and Coal Extract with Peroxytrifluoroacetic Acid: A mixture of trifluoroacetic acid and 90% hydrogen peroxide was prepared at 0°C. The coal or coal extract (0.25g) and 15 ml of the peroxytrifluoroacetic acid mixture were placed in a round-bottomed flask fitted with a dropping funnel into which was placed an additional volume of the peroxytrifluoroacetic acid mixture. The flask was heated in a water bath, and, at about 50°-60°C, a vigorous exothermic reaction began. As the reaction subsided, additional oxidant was added from the dropping funnel. This procedure was continued until the exothermic reaction had stopped. The coal samples consumed much more oxidant than did the extracts. The reactions were then worked up in the same manner as for the sulfides, except that it was necessary to filter mineral matter from the oxidized coal sample and it was not necessary to use platinum to destroy excess peroxide.

Table 1. OXIDATION OF COMMON ORGANIC SULFUR FUNCTIONAL GROUPS WITH $\text{CF}_3\text{CO}_3\text{H}$.

| COMPOUND | PRODUCTS (% yield) | |
|--------------------------|---|--|
| | $\text{CF}_3\text{CO}_3\text{H}/\text{H}_2\text{O}_2$, 25°, 15 min | $\text{CF}_3\text{CO}_3\text{H}/\text{H}_2\text{O}_2$, 60°, 5 h |
| Ph-SH | Ph-SO ₃ H (53%) Ph-S-S-Ph (5%) Ph-S-SO ₂ -Ph (5%) | Ph-SO ₃ H (92%) |
| Ph-S-S-Ph | Ph-S-S-Ph (91%) Ph-SO ₃ H (5%) | Ph-SO ₃ H (94%) |
| (n-butyl) ₂ S | (n-butyl) ₂ SO ₂ (99%) | (n-butyl) ₂ SO ₂ (99%) |
| dibenzothiophene | ^a | dibenzothiophene-5,5-dioxide (91%) |
| Ph-S-Ph | Ph-SO ₂ -Ph (95%) | Ph-SO ₂ -Ph (92%) |
| Ph-S-CH ₂ Ph | Ph-SO ₂ -CH ₂ Ph (99%) | Ph-SO ₂ -CH ₂ Ph (92%) |

^a partially oxidized, sulfide still detectable.

Table 2. OXIDATION OF ω -PHENYLALKYL PHENYL SULFIDES WITH $\text{CF}_3\text{CO}_3\text{H}^a$

| $\text{Ph-S-(CH}_2)_n\text{Ph} \longrightarrow \text{PhSO}_2(\text{CH}_2)_n\text{Ph} + \text{PhSO}_2(\text{CH}_2)_n\text{COOH} + \text{PhSO}_3\text{H}$ | | | |
|---|--------------------------|-------------------------------|--------------------------------|
| <u>n</u> | <u>sulfone yield</u> | <u>sulfone acid yield</u> | <u>sulfonic acid yield</u> |
| 0 | 92% | 0% | 0% |
| 1 | 91.5% | 0.5% | 0% |
| 2 | 55% | 8% | 16% |
| 3 ^b | 32% | 16% | 1% |

^a $\text{CF}_3\text{CO}_2\text{H}/\text{H}_2\text{O}_2 = 1.13/1$, 60° , 5 hr, see experimental for work-up procedure.

^bAt least 10 other compounds containing sulfur can be observed in the gc trace using flame photometric detection. If each is assumed to have one sulfur and an FID response factor which is the average of the sulfone and the sulfone acid, they would account for $37 \pm 12\%$ of the sulfurs.

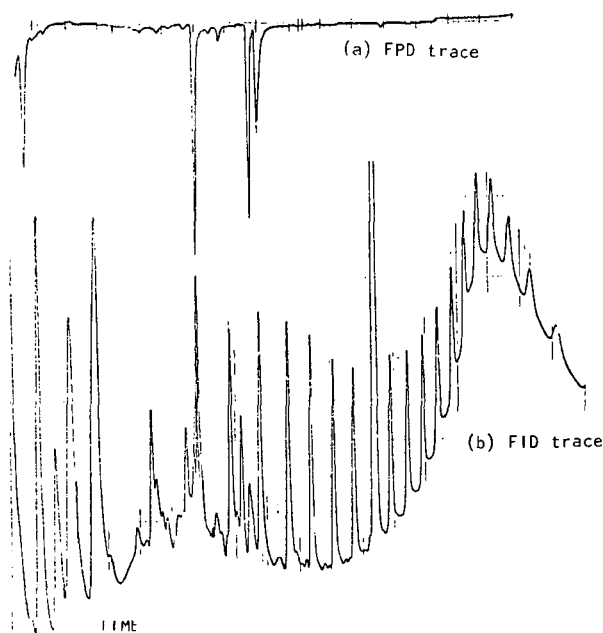


Figure 3. Gas Chromatogram of CH_2N_2 -Methylated Product of the Oxidation of Illinois #6 Coal by Peroxytrifluoroacetic Acid.
(a) Flame Photometric Detector; (b) Flame Ionization Detector

REFERENCES

1. For an excellent review of the area, see R. Hayatsu, R. G. Scott and R. E. Winans, "Oxidation of Coal," in Oxidation in Organic Chemistry. Part D, W. S. Trahanovsky, ed., Academic Press, New York, in press. We wish to thank the authors for providing a copy of their manuscript in advance of publication.
2. N. C. Deno, B. A. Greigger, L. A. Messer, M. D. Meyer, and S. G. Stroud, Tetrahedron Lett., 1703-4 (1977).
3. N. C. Deno, B. A. Greigger, and S. G. Stroud, Fuel, 57, 455-9 (1978).
4. N. C. Deno, B. A. Greigger, and S. G. Stroud, ACS Div. Fuel Chem., PREPRINTS, 23, 54-7 (1978).
5. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, and S. G. Stroud, Electric Power Research Institute AF-960, Project 779-16, Final Report, May, 1979.
6. N. C. Deno, K. W. Curry, J. E. Cwynar, A. D. Jones, R. D. Minard, T. Potter, W. G. Rakitsky, and K. Wagner, ACS Div. Fuel Chem., PREPRINTS, 25, #4, 103-10 (1980).
7. N. C. Deno, K. W. Curry, B. A. Greigger, A. D. Jones, W. G. Rakitsky, K. A. Smith, K. Wagner, and R. D. Minard, Fuel, 59, 694-8 (1980).
8. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, K. A. Smith, and R. D. Minard, Fuel, 59, 699-700 (1980).
9. N. C. Deno, B. A. Greigger, A. D. Jones, W. G. Rakitsky, D. D. Whitehurst, and T. O. Mitchell, Fuel, 50, 701-3 (1980).
10. R. Liotta and W. S. Hoff, J. Org. Chem., 45, 2887-90 (1980).
11. J. L. Kice and K. W. Bowers, J. Am. Chem. Soc., 84, 605-10 (1962)
12. C. J. M. Stirling, Int. J. Sulfur Chem., B, 6, 277-320 (1971).